METHOD FOR MANUFACTURING OPTICALLY ANISOTROPIC ELEMENT AND OPTICALLY ANISOTROPIC ELEMENT

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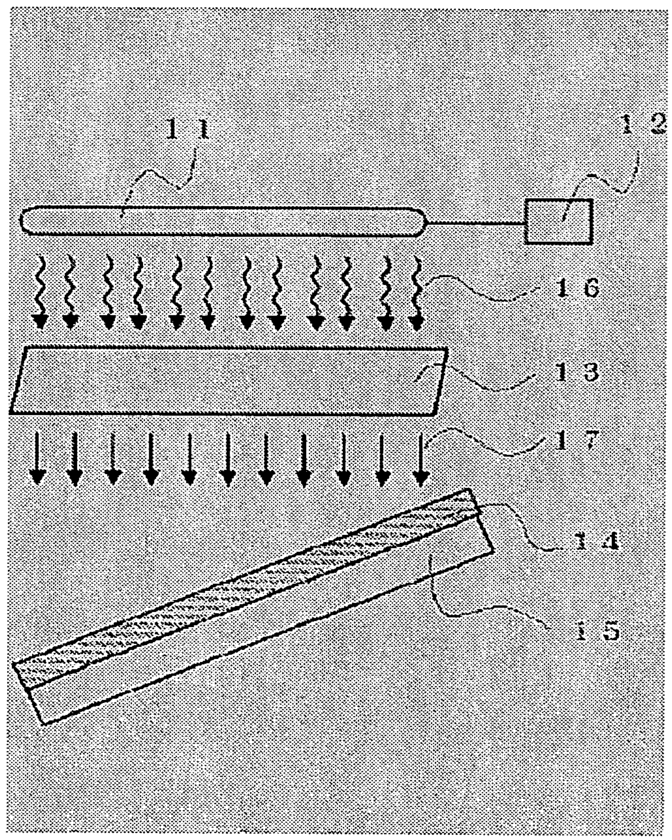
Abstract of **JP2003014928**

PROBLEM TO BE SOLVED: To provide an optically anisotropic element that optionally develops phase difference and its angle dependence by applying a molecular orientation to a film formed of a mixture of a photosensitive polymer and a low molecular weight compound on a uniaxial index ellipsoid layer and/or biaxial index ellipsoid layer by the irradiation of UV rays, and to provide a method for manufacturing the element. SOLUTION: The mixture of the photosensitive polymer and the low molecular weight compound is applied and formed into a film on a uniaxial index ellipsoid layer and/or biaxial index ellipsoid layer. When the film is exposed to linearly polarized light by using a device composed of a UV lamp, a power supply or an optical element (e.g. Glan-Taylor prism) which converts natural light into polarized light, the side chains in the photosensitive polymer anisotropically react with the light to induce phase difference. By irradiating the film in an oblique direction, the molecular alignment can be inclined in a desired direction. As a result, in the obtained optically anisotropic element, the angle dependence of the phase difference is controlled as desired.



DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the optical different direction component which made arbitration discover phase contrast and its angular dependence by what (for polarization exposure to be carried out) the ultraviolet rays (or light in which a completely-polarized-light component and an unpolarized light component are intermingled) of linearly polarized light nature are irradiated for on the film of the photosensitive polymer or the photosensitive polymer formed on the optically uniaxial index ellipsoid layer or/and the optically biaxial index ellipsoid layer, and the mixture of a low molecular weight compound, and its manufacturing method.
[0002]
[Description of the Prior Art] A phase contrast film is an optical different direction component which has the birefringence which is made to pass the linearly polarized light component which vibrates in the perpendicular direction of a main shaft mutually, and gives phase contrast required among these 2 components. Such an optical different direction component is utilized also for the liquid crystal display field, and especially the optical different direction component to which the optical axis inclined to the film plane can turn into an optical different direction component which is useful to angle-of-visibility expansion of a liquid crystal display as an optical compensation film.
[0003] The conventional technique of manufacturing such an optical different direction component is reported. For example, the optical different direction component which made the patent registration No. 2640083 carry out the inclination array of the discotheque liquid crystal with the rubbing orientation film and the method vacuum evaporationo orientation film of SiO slanting is indicated. Moreover, the optical different direction component constituted from JP,10-332933,A by the film which carried out the inclination array of the liquid crystallinity giant molecule which has forward form birefringence on the rubbing orientation film and the method vacuum evaporationo orientation film of SiO slanting, and the layer of negative form birefringence is indicated.
[0004] However, by the approach using the above orientation film, production processes, such as orientation down stream processing of the orientation film, a spreading process of a liquid crystal ingredient, and an orientation process, become complicated, and the manufacturing cost of an optical different direction component which made the optical axis of a large area incline becomes high. Moreover, the optical property of a liquid crystal display is various by design. In order to double the optical property of an optical different direction component and to acquire the angle-of-visibility expansion effectiveness, it is necessary to change the inclination of the orientation of the optical different direction component itself into such a variety of liquid crystal displays, and paint film conditions need accommodation of the surface tension of the orientation film and a liquid crystal ingredient, and to be changed for them. Furthermore, when the orientation film has effect which is not desirable on the display property of a liquid crystal display, it is necessary to remove this orientation film by approaches, such as exfoliation and the dissolution. Although the approach of carrying out the method vacuum evaporationo of the inorganic

dielectric of slanting is proposed as other methods of manufacturing the phase contrast film with which the optical axis inclined, in order to form the vacuum evaporationo film succeeding a long picture-like sheet top, technical problems, like equipment becomes large-scale occur. Moreover, in order to fully discover the angle-of-visibility expansion effectiveness of a liquid crystal display, it is necessary to combine with a layer, an optically uniaxial index ellipsoid layer, an optically biaxial index ellipsoid layer, etc. to which inclination orientation of such a liquid crystal component was carried out, and in order to stick these both layers with the adhesives which are optically uninfluential, there are problems, like a process becomes complicated.

[0005]

[Problem(s) to be Solved by the Invention] It is remarkably difficult for the optical different direction component produced by the extension orientation of a high polymer film for the orientation of a molecule to be restricted in the extension direction and to make an optical axis incline. Neither by the approach of on the other hand making a liquid crystallinity compound arranging on the base material which carried out orientation processing, nor the approach of carrying out the method vacuum evaporationo of the inorganic dielectric of slanting, although it is possible to produce the optical different direction component which made the optical axis incline, the optical different direction component which made the optical axis of a large area incline by low cost can be obtained. Furthermore, for fully discovering the angle-of-visibility expansion effectiveness of a liquid crystal display, it may use combining an optically uniaxial index ellipsoid layer or/and an optically biaxial index ellipsoid layer, it is necessary to stick this layer with adhesives etc., and a process becomes complicated. By this invention, the optical different direction component suitable for mass production method and its manufacturing method are offered at a simple process.

[0006]

[Means for Solving the Problem] By the manufacture approach (optical different direction component to depend) of the optical different direction component of this invention Form the film of a photosensitive polymer, or a photosensitive polymer and the mixture of a low molecular weight compound on an optically uniaxial index ellipsoid layer or/and an optically biaxial index ellipsoid layer, and by carrying out polarization exposure Since the optical anisotropic layer to which arbitration was made to incline and orientation of the optical axis was carried out can be formed on an optically uniaxial index ellipsoid layer or/and an optically biaxial index ellipsoid layer, the approach of manufacturing an optical different direction component effective in angle-of-visibility expansion of a liquid crystal display at a simple process is realized.

[0007]

[Embodiment of the Invention] Below, the detail of this invention is explained. The photosensitive polymer used for this invention is a giant molecule which has a side chain including the structure which combined substituents, such as a biphenyl currently used abundantly as a meso gene component of a liquid crystallinity giant molecule, terphenyl, phenyl benzoate, and an azobenzene, and photosensitive radicals, such as a cinnamic acid radical (or the derivative radical), and has structures, such as a hydrocarbon, acrylate, methacrylate, maleimide, N-phenyl maleimide, and a siloxane, in a principal chain. It is also possible to carry out copolymerization of the unit which has the side chain which the copolymer of the unit which has the side chain with which the homopolymer which consists of the same repeat unit differs from structure is sufficient as this polymer, or does not contain a photosensitive radical. Moreover, the low molecular weight compound to mix is also a compound which has substituents, such as a biphenyl currently used abundantly as a meso gene component, terphenyl, phenyl benzoate, and an azobenzene, and has the crystallinity which did not mind functional groups, such as this meso gene component, an allyl compound, acrylate, methacrylate, and a cinnamic acid radical (or the derivative radical), through the flexibility component, but was combined, or liquid crystallinity. When mixing these low molecular weight compounds, it is also possible not to restrict but to mix two or more sorts of compounds with a single compound.

[0008] This photosensitive polymer, or a photosensitive polymer and the mixture of a low molecular

weight compound is applied on an optically uniaxial index ellipsoid layer or/and an optically biaxial index ellipsoid layer, and the spreading film is formed. As the optically uniaxial index ellipsoid layer used here or/and an optically biaxial index ellipsoid layer, one shaft or the thing which carried out biaxial stretching, the thing which made a photosensitive ingredient like this invention discover a Mitsuteru putting birefringence are mentioned in polymeric materials, such as a polycarbonate and triacetyl cellulose. However, if it has a desired optical property, it will not be limited to these.

[0009] Change which irradiates the light L of linearly polarized light nature (it has the oscillating direction shown by the arrow head m) at the spreading film 20 which applied and formed this kind of photosensitive polymer and the mixture of a low molecular weight compound on the substrate by drawing 2 and drawing 3 , and is produced in the spreading film of a case (orientation processing of heating etc. was performed again) is shown (before an exposure = after [drawing 2 , an exposure, and orientation processing] = drawing 3).

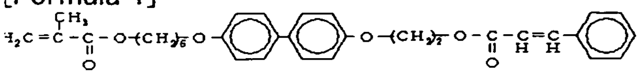
[0010] The spreading film 20 is isotropy at the time of film production, and the photosensitive side-chain section (shown by the prolate ellipsoid) and the photosensitive low molecular weight compound (shown by the cylinder) of a polymer have not turned to the specific direction. A condition in case the light L of linearly polarized light nature irradiates (polarization exposure) is explained based on drawing 2 from specification in the spreading film 20. In the spreading film 20, side-chain 2b of side-chain 2a of photosensitive high arrangement which is in the sense corresponding to a perpendicular direction to the oscillating direction m and exposure Mitsuyuki line writing direction of exposure light, and photosensitive scarce arrangement exists. Moreover, low-molecular-weight-compound 2c lives together disorderly. If polarization exposure of this film is carried out, the photoreaction of side-chain 2a of the arrangement which is in the sense corresponding to a perpendicular direction to the electric-field oscillating direction and travelling direction of exposure light will advance preferentially.

[0011] Drawing 3 shows the film 30 after a Mitsuteru putting reaction advances on the film 20 of drawing 2 . By the molecular motion after polarization exposure, as shown in drawing 3 , orientation is carried out in the same direction as side-chain 3a (2a) which carried out the photoreaction also of side-chain 3b (2b) and low-molecular-weight-compound 3c (2c) of the polymer which did not start the photoreaction. Consequently, in the whole spreading film, the side chain of a polymer and the molecule of a low molecular weight compound carry out orientation perpendicularly to the electric-field oscillating direction and exposure Mitsuyuki line writing direction of the linearly polarized light which were irradiated, induction of the birefringence is carried out and it serves as an optical anisotropic layer. By performing this polarization exposure from across to a film surface, arbitration can be made to be able to incline and orientation of the optical axis can be carried out. Consequently, the optical anisotropic layer which set up the optical axis towards desired can form on an optically uniaxial index ellipsoid layer or/and an optically biaxial index ellipsoid layer. In order to advance the photoreaction, the exposure of the light of wavelength to which the part of a photosensitive radical can react is required. Although this wavelength changes also with classes of photosensitive radical, generally it is 200 to 500 nm, and its effectiveness of 250 to 400 nm is high especially in many cases.

[0012] The orientation by the molecular motion after the above-mentioned polarization exposure is promoted by heating a substrate. Whenever [stoving temperature / of a substrate] is lower than the softening temperature of the part which carried out the photoreaction, and it is desirable that it is higher than the softening temperature of the side chain which did not carry out the photoreaction, and a low molecular weight compound. Thus, if the film which carried out polarization exposure and which carried out orientation under the film to which it heated and orientation of the unreacted side chain was carried out, or heating is cooled below to the softening temperature of this macromolecule after carrying out polarization exposure, a molecule will be frozen and the orientation film of this invention will be obtained. When the low molecular weight compound has heat and/or photoreaction nature to low molecular weight compounds or this polymer, since orientation is fixed firmly, heat-resistant improvement is expected. In such a case, it is necessary to stop light exposure, or to adjust reactivity and to control the consistency of a photoreaction point not to bar the molecular motion at the time of reorientation.

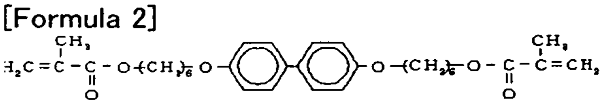
[0013] While a low molecular weight compound has the effectiveness which will bloom cloudy if it is optimum dose, and controls whenever, if it adds superfluously, it will bloom cloudy, and causes the increment in whenever, and the fall of a stacking tendency. although based also on a photosensitive polymer or the class of low molecular weight compound from such a viewpoint -- a low molecular weight compound -- 0.1wt(s)% - 80wt% -- although an optical different direction component can be manufactured even if it adds, it is desirable that it is 5wt(s)% - 50wt% preferably. Here, when a photosensitive polymer and the compatibility of a low molecular weight compound are not enough, with heating of the substrate after the time of film production, or polarization exposure, the crystal of the magnitude which can carry out induction of the dispersion of phase separation or the light is generated, and it becomes the cause of the increment in whenever [cloudy]. In order to control generation of this phase separation and microcrystal, it is necessary to adjust the compatibility of a polymer and a low molecular weight compound. As a scale of this compatibility Polymer Engineering and Evaporation energy (deltaEv) which is indicated by Science, Vol.7, and No.2,147 (1974), and the soluble parameter (sigma) computed with a formula (1) from molecular volume (V) expedient -- it can use -- the ratio of the soluble parameter (sigma) of a polymer and a low molecular weight compound -- it has become clear by experiment that it can control generation of phase separation or a microcrystal effectively when the range of :z is 0.93< z<1.06.
sigma=(deltaEv/V) 1/2 Formula (1)
[0014] Moreover, whenever [cloudy] will be [become] easy to increase, if thickness becomes thick and molecular orientation is confused. In order to control whenever [this cloudiness], it is effective to make thickness thin. Although it will lead to the fall of phase contrast if thickness is made thin, by applying an ingredient solution to both sides of an optically uniaxial index ellipsoid layer or/and an optically biaxial refractive-index ellipse layer, and making thickness of a hit thin further, it blooms cloudy, without reducing the phase contrast of the whole optical different direction component, and whenever can be controlled. Moreover, the approach of carrying out the laminating of the film is mentioned as the technique of acquiring big phase contrast. In this case, although the laminating of the ingredient solution is applied and carried out on the film which produced the film previously and carried out polarization exposure, in order to prevent destruction of this film formed previously, it is effective to dissolve and use a polymer and a low molecular weight compound for the solvent which lowered solubility. Moreover, phase contrast can also be made to discover efficiently by carrying out polarization exposure from the both sides from the optically uniaxial index ellipsoid layer side of the film side of a surface photosensitive polymer and the mixture of a low molecular weight compound, and a rear face, or/and an optically biaxial index ellipsoid layer side (or film side of a photosensitive polymer on the back and the mixture of a low molecular weight compound). Although what kind of ingredient is sufficient as the optically uniaxial index ellipsoid layer or/and optically biaxial index ellipsoid layer to be used as long as it has the permeability of the light of wavelength to which a photosensitive polymer can react, there is so little light exposure that light transmittance is high, they end, and become advantageous on a production process.
[0015] The optical property of the optical anisotropic layer with which the optical axis inclined, an optically uniaxial index ellipsoid layer, or/and an optically biaxial index ellipsoid layer is adjusted by the optical property of the liquid crystal display with which it is equipped with this optical different direction component. When the direction of orientation of an optical anisotropic layer and an optically uniaxial index ellipsoid layer where the optical axis inclined is made to intersect perpendicularly and it is made to arrange, the optical different direction component which has the optical property same with having carried out inclination orientation of the index ellipsoid which has a negative birefringence can also be adjusted by adjusting each phase contrast. It is necessary to design the phase contrast of an optical different direction component in optical compensation of a liquid crystal display in consideration of the phase contrast of all the optical system that constitutes these equipment including a polarizing plate.
[0016] The synthetic approach about the example of the raw material compound in this invention is shown below.
(Monomer 1) The 4-hydroxy-4'-hydroxy ethoxy biphenyl was compounded by heating 4, and 4'-biphenyl

diol and 2-chloroethanol under alkali conditions. 1 and 6-dibromo hexane was made to react to this product under alkali conditions, and the 4-(6-BUROMO hexyloxy)-4'-hydroxy ethoxy biphenyl was compounded. Subsequently, lithium methacrylate was made to react and the 4-(2-hydroxy ethoxy)-4'-(6-methacryloyloxy hexyloxy) biphenyl was compounded. Finally, the phenylacrylyl chloride was added to the bottom of a basic condition, and the methacrylic ester shown in a chemical formula 1 was compounded.
[Formula 1]



･･･ (化学式 1)

[0017] (Polymer 1) The monomer 1 was dissolved into the tetrahydrofuran and the polymer 1 was obtained by adding and carrying out the polymerization of the azobisuisobutironitoriru (azobisisobutyronitril) as a reaction initiator. This polymer 1 presented liquid crystallinity in the temperature field of 47 to 75 degree C.
[0018] (Low molecular weight compound 1) 4, 4'-biphenyl diol and 1, and 6-dibromo hexane were made to react under alkali conditions, and 4 and a 4'-screw (6-BUROMO hexyloxy) biphenyl were compounded. Subsequently, lithium methacrylate was made to react and the low molecular weight compound 1 shown in a chemical formula 2 was compounded by carrying out column purification of the product.
[Formula 2]



･･･ (化学式 2)

[0019]
[Example] The example of the manufacture approach in the case of producing the optical different direction component of this invention by carrying out polarization exposure of the ultraviolet radiation of linearly polarized light nature (equipment) is shown in drawing 1 . However, the manufacture approach of the optical different direction component of this invention is not limited to this. The disorderly light 16 generated with the ultraviolet ray lamp 11 excited by the power source 12 has an optical element 13 (for example, the Gulan Taylor prism), is changed into the ultraviolet rays 17 of linearly polarized light nature, and irradiates the film 14 of the photosensitive polymer or the photosensitive polymer applied on the film of the optically uniaxial index ellipsoid produced by approaches, such as extension, or/and the film 15 of an optically biaxial index ellipsoid (coat), and the mixture of a low molecular weight compound. An example 1 and an example 2 are examples which produced the optical different direction component according to the manufacturing method of this invention. SENARUMON for which the angular dependence of the phase contrast of this optical different direction component used the polarizer, the quarter-wave length plate, and the analyzer -- it asked by measuring the extinction angle of an analyzer, rotating a test portion by predetermined optical system by law.
[0020] (Example 1)
(1) 3.75% of the weight of the polymer 1 and 1.25% of the weight of the low molecular weight compound 1 were dissolved in the dichloroethane, and the phase contrast within a field applied and produced the film by the thickness of about 1.5 micrometers on the polycarbonate film which is 81nm.
(2) It is made in agreement [the electric-field oscillating direction] with the extension direction of a polycarbonate film, and it irradiated the ultraviolet rays which used the Gulan Taylor prism and were changed into the film production side side of the film which produced the film at the linearly polarized light two times 100 mJ/cm from the direction which inclines 20 degrees to the direction of a film production side normal.
(3) Then, the 2180 200 mJ/cm symmetry was irradiated from the polycarbonate film rear-face side.
(4) After heating the film (film) which finished the exposure at 100 degrees C, it cooled to the room

temperature.
Thus, the phase contrast of the obtained optical different direction component had angular dependence as shown in drawing 4 .
[0021] (Example 2)
(1) 3.75% of the weight of the polymer 1 and 1.25% of the weight of the low molecular weight compound 1 were dissolved in the dichloroethane, and the phase contrast within a field applied and produced the film by the thickness of about 1.5 micrometers on the polycarbonate film which is 81nm.
(2) From the direction where it is made for the extension direction of a polycarbonate film and the electric-field oscillating direction to cross at right angles in, and it inclines the ultraviolet rays which used the Gulan Taylor prism and were changed into the film production side side of the film which produced the film at the linearly polarized light 20 degrees to the direction of a normal on the front face of film production to 100 mJ/cm2 exposure
(3) Then, the 2180 200 mJ/cm symmetry was irradiated from the polycarbonate film rear-face side.
(4) After heating the film (film) which finished the exposure at 100 degrees C, it cooled to the room temperature.
Thus, the phase contrast of the obtained optical different direction component had angular dependence as shown in drawing 5 .
[0022] the Casio make -- the optical different direction component (film) 61 according to an example 1 as the polarization sheet of liquid crystal color-television EV-510 is removed and it is shown in drawing 6 , and 61' -- a liquid crystal cell 62 -- up and down -- one-sheet each lamination -- subsequently it stuck one upper and lower sides at a time the polarization sheet 63 and 63'. In drawing, a and a' shows the inclination direction of an index ellipsoid, b and b' shows the extension direction of a polycarbonate film, c and c' shows the direction of a pre tilt of a liquid crystal cell, and d and d' shows the absorption shaft orientations of a polarization sheet. The optical different direction component 61 and 61' come to carry out the laminating of slanting orientation layer 61a and 61a' to base material 61b and 61b', respectively. Liquid crystal color television was driven with such a configuration, the place where a white display and the contrast ratio at the time of doing the black display of become 5 was defined as the angle of visibility, and the angle-of-visibility property of the right-and-left vertical direction was measured. TOPCON BM-5A was used for measurement of a contrast ratio. A result is collectively shown in Table 1.

[Table 1]

表1

フィルム	視野角(°)			
	上	下	左	右
実施例1	5	48	63	53
実施例2	5	42	60	52
比較例(偏光シートのみ)	5	20	40	33

In the optical different direction component of this invention, and its manufacturing method, by irradiating ultraviolet rays further, the component which produced phase contrast by polarization exposure can be made to be able to promote the photoreaction of an unreacted photosensitive radical, and the orientation in a component can be firmly fixed to it. Such an optical different direction component was excellent in thermal resistance and light stability, and enough for practical use. The angle-of-visibility expansion effectiveness was checked for the optical different direction component of an example 1 and an example 2 in the left, the right, and a direction the bottom.
[Effect of the Invention] Although the complicated process was required for the production process of the optical element toward which the optical axis which can be utilized as an optical different direction component for angle-of-visibility expansion in a liquid crystal display inclined conventionally , manufacture of an optical different direction component was attained by simple actuation of carrying out polarization exposure from across , by this invention at the film of the photosensitive polymer or the photosensitive polymer applied to the optically uniaxial index ellipsoid layer or/and the optically biaxial index ellipsoid layer , and the mixture of a low molecular weight compound .
[0023]

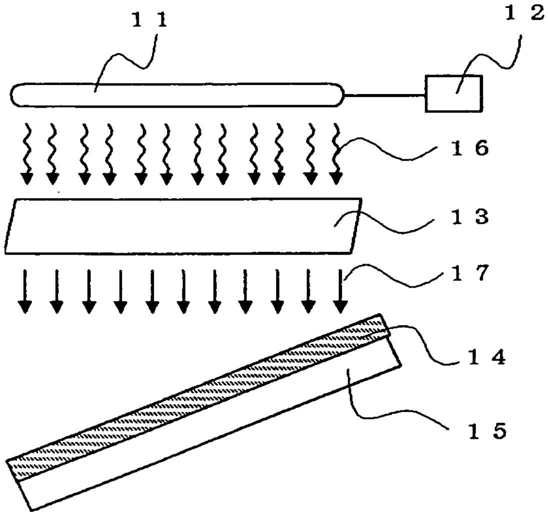
[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of the optical different direction component characterized by forming the film formed by the photosensitive polymer, or a photosensitive polymer and the mixture of a low molecular weight compound on an optically uniaxial index ellipsoid layer or/and an optically biaxial index ellipsoid layer, and forming in arbitration an inclination and the optical anisotropic layer which carried out orientation for an optical axis by carrying out an optical exposure.
[Claim 2] The manufacture approach of an according to claim 1 optical different direction component that the optical exposure to the film formed by said photosensitive polymer, or a photosensitive polymer and the mixture of a low molecular weight compound is characterized by being made from membranous front rear-face both directions.
[Claim 3] The manufacture approach of claim 1 characterized by including the process which heats and/or cools the film formed by said photosensitive polymer, or a photosensitive polymer and the mixture of a low molecular weight compound thru/or an according to claim 2 optical different direction component.
[Claim 4] The manufacture approach of the according to claim 1 to 3 optical different direction component characterized by including the process which constructs a bridge in the photosensitive polymer or photosensitive low molecular weight compound which constitutes said optical anisotropic layer.
[Claim 5] The optical different direction component characterized by being manufactured by the manufacture approach according to claim 1 to 4.
[Claim 6] The according to claim 5 optical different direction component characterized by said photosensitive polymer having liquid crystallinity.

[Translation done.]

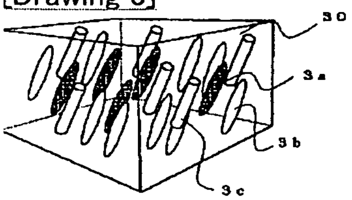
Drawing selection Representative drawing



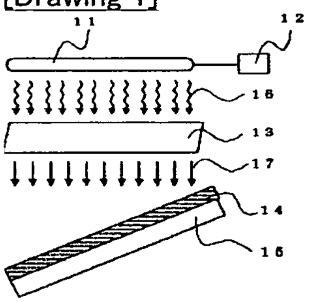
[Translation done.]

DRAWINGS

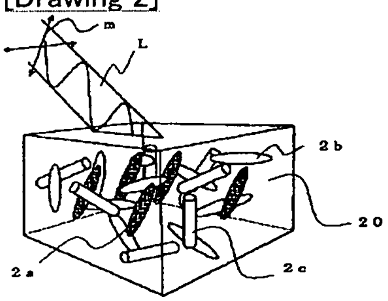
[Drawing 3]



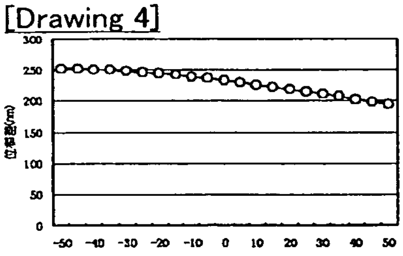
[Drawing 1]



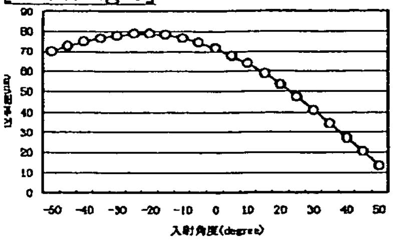
[Drawing 2]



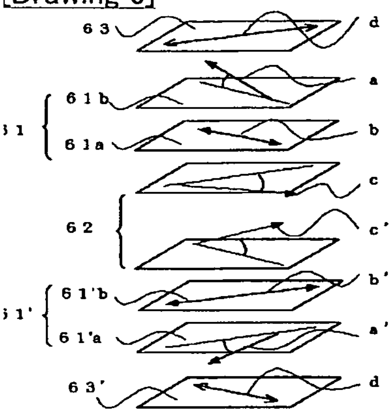
[Drawing 4]



[Drawing 5]



[Drawing 6]



[Translation done.]

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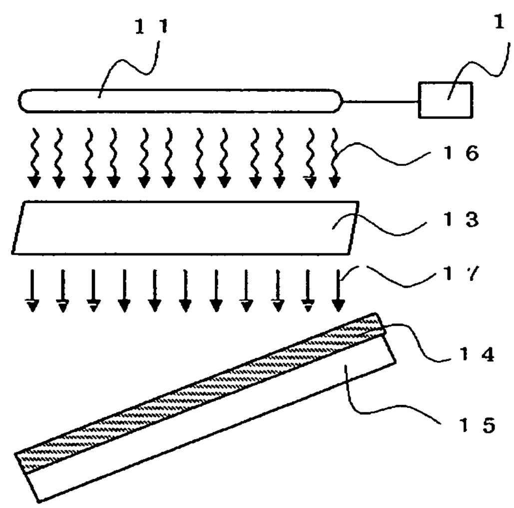
(54)【発明の名称】　光学異方素子の製造方法、および光学異方素子

(57)【要約】
【目的】一軸性屈折率楕円体層または／および二軸性屈折率楕円体層上に形成した感光性の重合体と低分子化合物の混合体の膜に、紫外線を照射することによって、分子配向させ位相差とその角度依存性を任意に発現させた光学異方素子および、その製造法の実現。
【構成】感光性の重合体と低分子化合物の混合体を一軸性屈折率楕円体層または／および二軸性屈折率楕円体層上に塗布し製膜する。該膜に、紫外線ランプ、電源あるいは、自然光を偏光に変換する光学素子（例えばグランテーラープリズム）からなる装置を用い、偏光露光すると、感光性の重合体の側鎖が異方的に光反応し、位相差が誘起される。この照射を斜め方向から行なうことによって、分子配向を任意に傾斜させることができ、その結果、位相差の角度依存性を所望に設定した光学異方素子を提供できる。



【特許請求の範囲】

【請求項１】　感光性の重合体ないしは感光性の重合体と低分子化合物の混合体で形成された膜を、一軸性屈折率楕円体層または／および二軸性屈折率楕円体層上に形成し、光照射することによって、光軸を任意に傾斜、配向させた光学異方層を形成することを特徴とする、光学異方素子の製造方法。

【請求項２】　前記感光性の重合体ないしは感光性の重合体と低分子化合物の混合体で形成された膜に対する光照射が、膜の表裏面両方向からなされることを特徴とする、請求項１に記載の光学異方素子の製造方法。

【請求項３】　前記感光性の重合体ないしは感光性の重合体と低分子化合物の混合体で形成された膜を加熱、および／または冷却する工程を含むことを特徴とする、請求項１ないし請求項２に記載の光学異方素子の製造方法。

【請求項４】　前記光学異方層を構成する感光性の重合体ないしは低分子化合物を架橋する工程を含むことを特徴とする、請求項１～請求項３に記載の光学異方素子の製造方法。

【請求項５】　請求項１～請求項４に記載の製造方法によって製造されたことを特徴とする、光学異方素子。

【請求項６】　前記感光性の重合体が液晶性を有することを特徴とする、請求項５に記載の光学異方素子。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、一軸性屈折率楕円体層または／および二軸性屈折率楕円体層上に形成した感光性の重合体ないしは感光性の重合体と低分子化合物の混合体の膜に、直線偏光性の紫外線（ないしは、完全偏光成分と非偏光成分が混在する光）を照射する（偏光露光する）ことによって、位相差とその角度依存性を任意に発現させた光学異方素子および、その製造法に関するものである。

【０００２】

【従来の技術】位相差フィルムは、互いに垂直な主軸方向に振動する直線偏光成分を通過させ、この二成分間に必要な位相差を与える複屈折を有する光学異方素子である。このような光学異方素子は液晶表示分野にも活用されてきており、特に、光軸がフィルム面に対し傾いた光学異方素子は光学補償フィルムとして液晶表示装置の視野角拡大に役立つ光学異方素子となり得る。

【０００３】このような光学異方素子を製造する従来技術が報告されている。例えば、特許登録２６４００８３号には、ラビング配向膜、ＳｉＯ斜方蒸着配向膜によりディスコティック液晶を傾斜配列させた光学異方素子が記載されている。また、特開平１０－３３２９３３号では、正の複屈折性を有する液晶性高分子をラビング配向膜、ＳｉＯ斜方蒸着配向膜上に傾斜配列させたフィルムと負の複屈折性の層とによって構成される光学異方素子が記載されている。

【０００４】しかしながら、上記のような配向膜を用いる方法では、配向膜の配向処理工程、液晶材料の塗布工程、配向工程など製造工程が煩雑となり、大面積の光軸を傾斜させた光学異方素子の製造費が高くなる。また、液晶表示装置は設計により光学特性は多種多様である。このような多種多様な液晶表示装置に、光学異方素子の光学特性を合わせ、視野角拡大効果を得るには、光学異方素子自体の配向の傾きを変える必要もあり、配向膜と液晶材料の表面張力の調節や塗膜条件の変更が必要である。更には、配向膜が液晶表示装置の表示特性に好ましくない影響を与える場合には、剥離や溶解などの方法により該配向膜を除去する必要がある。光軸の傾いた位相差フィルムを製造する他の方法として、無機誘電体を斜方蒸着する方法が提案されているが、長尺状シート上に連続して蒸着膜を形成するには、装置が大掛かりになるなどの課題がある。また、液晶表示装置の視野角拡大効果を十分に発現するには、このような液晶成分を傾斜配向させた層と一軸性屈折率楕円体層または／および二軸性屈折率楕円体層などと組み合わせる必要があり、該両層を光学的に影響のない接着剤で貼り合わせるため工程が煩雑になるなどの問題がある。

【０００５】

【発明が解決しようとする課題】高分子フィルムの延伸配向によって作製された光学異方素子は、分子の配向が延伸方向に限られ光軸を傾斜させることが著しく困難である。一方、配向処理した基材上で液晶性化合物を配列させる方法や無機誘電体を斜方蒸着する方法では、光軸を傾斜させた光学異方素子を作製することは可能であるが、低コストで大面積の光軸を傾斜させた光学異方素子を得ることはできない。更には、液晶表示装置の視野角拡大効果を十分に発現するには一軸性屈折率楕円体層または／および二軸性屈折率楕円体層と組み合わせて用いる場合があり、該層を接着剤などで貼り合わせる必要があり工程が煩雑となる。本発明では、簡便な工程で、大量生産に適する光学異方素子およびその製造法を提供する。

【０００６】

【課題を解決する手段】本発明の光学異方素子の製造方法（による光学異方素子）では、感光性の重合体ないしは感光性の重合体と低分子化合物の混合体の膜を一軸性屈折率楕円体層または／および二軸性屈折率楕円体層上に形成し、偏光露光することによって、光軸を任意に傾斜させて配向させた光学異方層を一軸性屈折率楕円体層または／および二軸性屈折率楕円体層上に形成できるので、液晶表示装置の視野角拡大に有効な光学異方素子を簡便な工程で製造する方法を実現する。

【０００７】

【発明の実施の形態】以下に、本発明の詳細を説明する。本発明に用いられる感光性の重合体は、液晶性高分

子のメソゲン成分として多用されているビフェニル、ターフェニル、フェニルベンゾエート、アゾベンゼンなどの置換基と、桂皮酸基（または、その誘導体基）などの感光性基を結合した構造を含む側鎖を有し、炭化水素、アクリレート、メタクリレート、マレイミド、N－フェニルマレイミド、シロキサンなどの構造を主鎖に有する高分子である。該重合体は同一の繰り返し単位からなる単一重合体または構造の異なる側鎖を有する単位の共重合体でもよく、あるいは感光性基を含まない側鎖を有する単位を共重合させることも可能である。また、混合する低分子化合物も、メソゲン成分として多用されているビフェニル、ターフェニル、フェニルベンゾエート、アゾベンゼンなどの置換基を有し、該メソゲン成分とアリル、アクリレート、メタクリレート、桂皮酸基（または、その誘導体基）などの官能基を、屈曲性成分を介してまたは、介さず結合した結晶性または、液晶性を有する化合物である。これら低分子化合物を混合する場合、単一の化合物のみとは限らず複数種の化合物を混合することも可能である。

【0008】該感光性の重合体ないしは感光性の重合体と低分子化合物の混合体を一軸性屈折率楕円体層または／および二軸性屈折率楕円体層上に塗布し塗布膜を形成する。ここで用いられる一軸性屈折率楕円体層または／および二軸性屈折率楕円体層としては、ポリカーボネートやトリアセチルセルロースなどの高分子材料を一軸または二軸延伸したもの、本発明のような感光性材料に光照射し複屈折を発現させたものなどが挙げられる。但し、所望の光学特性を有するものであればこれらに限定されるものではない。

【0009】図2および図3によって、この種の感光性の重合体と低分子化合物の混合体を基板上に塗布して形成した塗布膜20に直線偏光性の光L（矢印mで示す振動方向を有する）を照射し（また加熱等の配向処理をおこなった）場合の、塗布膜内に生じる変化を示す（照射前＝図2、照射、配向処理後＝図3）。

【0010】塗布膜20は、製膜時には等方性であり、感光性の重合体の側鎖部（長楕円で示される）および低分子化合物（円柱で示される）は特定方向を向いていない。塗布膜20にある特定方向から直線偏光性の光Lが照射（偏光露光）する場合の状態を図2に基づいて説明する。塗布膜20中では、照射光の振動方向mかつ照射光進行方向に対し垂直方向に対応した向きにある感光性の高い配置の側鎖2aと、感光性の乏しい配置の側鎖2bが存在している。また、低分子化合物2cが無秩序に共存している。この膜を偏光露光すると、照射光の電界振動方向かつ進行方向に対し垂直方向に対応した向きにある配置の側鎖2aの光反応が優先的に進行する。

【0011】図3は、図2の膜20に光照射し反応が進行した後の膜30を示す。偏光露光後の分子運動により、図3に示すように、光反応を起こさなかった重合体の側鎖3b（2b）と低分子化合物3c（2c）も光反応した側鎖3a（2a）と同じ方向に配向する。その結果、塗布膜全体において、照射した直線偏光の電界振動方向かつ照射光進行方向に対し垂直方向に重合体の側鎖と低分子化合物の分子が配向し、複屈折が誘起され光学異方層となる。この偏光露光を膜面に対して斜め方向から行なうことによって、光軸を任意に傾斜させて配向させることができる。その結果、光軸を所望の方向に設定した光学異方層が一軸性屈折率楕円体層または／および二軸性屈折率楕円体層上に形成できる。光反応を進めるには、感光性基の部分が反応し得る波長の光の照射を要する。この波長は、感光性基の種類によっても異なるが、一般に200－500nmであり、中でも250－400nmの有効性が高い場合が多い。

【0012】前述の偏光露光後の分子運動による配向は、基板を加熱することにより促進される。基板の加熱温度は、光反応した部分の軟化点より低く、光反応しなかった側鎖と低分子化合物の軟化点より高いことが望ましい。このように偏光露光したのち加熱し未反応側鎖を配向させた膜または加熱下で偏光露光し配向させた膜を該高分子の軟化点以下まで冷却すると分子が凍結され、本発明の配向膜が得られる。低分子化合物が低分子化合物同士、もしくは該重合体に対して熱および／または光反応性を有している場合には、配向が強固に固定されるため耐熱性の向上が期待される。このような場合、再配向時の分子運動を妨げないよう、露光量を抑えるか反応性を調整するなどして、光反応点の密度を制御する必要がある。

【0013】低分子化合物は、適量ならば曇り度を抑制する効果がある反面、過剰に添加すると曇り度の増加、配向性の低下を引き起こす。このような観点から、感光性の重合体または低分子化合物の種類にもよるが、低分子化合物を0．1wt％～80wt％添加しても光学異方素子は製造可能であるが、好ましくは5wt％～50wt％であることが望ましい。ここで、感光性の重合体と低分子化合物の相溶性が十分でない場合には、製膜時ないしは偏光露光後の基板の加熱によって相分離や可視光の散乱を誘起しうる大きさの結晶を生成し曇り度の増加の原因となる。この相分離や微結晶の生成を抑制するためには、重合体と低分子化合物の相溶性を調節する必要がある。この相溶性の尺度としてPolymer Engineering and Science, Vol. 7, No. 2, 147 (1974) に記載されているような蒸発エネルギー（ΔEv）と分子容（V）から計算式（1）をもって算出される溶解性パラメーター（σ）を便宜的に利用でき、重合体と低分子化合物の溶解性パラメーター（σ）の比：zが、$0.93 < z < 1.06$の範囲である場合に相分離や微結晶の生成を効果的に抑制できることが実験により判明している。

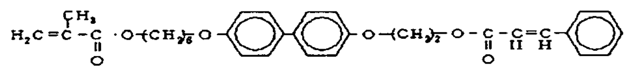
$$\sigma = (\Delta Ev / V)^{1/2} \qquad \text{計算式（1）}$$

【0014】また、曇り度は、膜厚が厚くなり分子配向が乱れると増加しやすくなる。該曇り度を抑制するには、膜厚を薄くすることが有効である。膜厚を薄くすると位相差の低下に繋がるが、一軸性屈折率楕円体層または／および二軸性屈折率楕円層の両面に材料溶液を塗布し、一層当りの膜厚を薄くすることにより、光学異方素子全体の位相差を低下させることなく曇り度を抑制できる。また、大きな位相差を得る手法として、膜を積層する方法が挙げられる。この場合、先に製膜し、偏光露光した膜上に材料溶液を塗布し積層するが、この先に形成された膜の破壊を防ぐために、溶解性を下げた溶媒に重合体および低分子化合物を溶解し用いることが有効である。また、表面の感光性の重合体と低分子化合物の混合体の膜側および裏面の一軸性屈折率楕円体層または／および二軸性屈折率楕円体層側（もしくは、裏面の感光性の重合体と低分子化合物の混合体の膜側）からの両側より偏光露光することによって、効率よく位相差を発現させることもできる。用いる一軸性屈折率楕円体層または／および二軸性屈折率楕円体層は感光性の重合体の反応しうる波長の光の透過性を有している限りどのような材料でも良いが、光透過率が高い程、露光量が少なくて済み、製造工程上有利となる。

【0015】光軸の傾斜した光学異方層と一軸性屈折率楕円体層または／および二軸性屈折率楕円体層の光学特性は、該光学異方素子が装着される液晶表示装置の光学特性によって調節される。光軸の傾斜した光学異方層と一軸性屈折率楕円体層の配向方向を直交させて配置させた場合、各々の位相差を調節することにより、負の複屈折を有する屈折率楕円体を傾斜配向させたのと同様な光学特性を有する光学異方素子を調整することもできる。液晶表示装置の光学補償には、偏光板を含め該装置を構成する全ての光学系の位相差を考慮し光学異方素子の位相差を設計する必要がある。

【0016】本発明における原料化合物の例に関する合成方法を以下に示す。
（単量体1）4，4’－ビフェニルジオールと2－クロロエタノールを、アルカリ条件下で加熱することにより、4－ヒドロキシ－4’－ヒドロキシエトキシビフェニルを合成した。この生成物に、アルカリ条件下で1，6－ジブロモヘキサンを反応させ、4－（6－ブロモヘキシルオキシ）－4’－ヒドロキシエトキシビフェニルを合成した。次いで、リチウムメタクリレートを反応させ、4－（2－ヒドロキシエトキシ）－4’－（6－メタクリロイルオキシヘキシルオキシ）ビフェニルを合成した。最後に、塩基性の条件下において、塩化シンナモイルを加え、化学式1に示されるメタクリル酸エステルを合成した。

【化1】

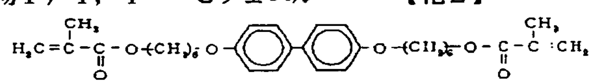


・・・(化学式 1)

【0017】（重合体1）単量体1をテトラヒドロフラン中に溶解し、反応開始剤としてAIBN（アゾビスイソブチロニトリル）を添加して重合することにより重合体1を得た。この重合体1は、47－75℃の温度領域において、液晶性を呈した。

【0018】（低分子化合物1）4，4’－ビフェニルジオールと1，6－ジブロモヘキサンを、アルカリ条件下で反応させ、4，4’－ビス（6－ブロモヘキシルオキシ）ビフェニルを合成した。次いで、リチウムメタクリレートを反応させ、生成物をカラム精製することにより化学式2に示される低分子化合物1を合成した。

【化2】



・・・(化学式 2)

【0019】
【実施例】図1には、本発明の光学異方素子を直線偏光性の紫外光を偏光露光することにより作製する場合の製造方法（装置）の例を示す。但し、本発明の光学異方素子の製造方法はこれに限定されるものではない。電源12によって励起された紫外線ランプ11で発生した無秩序光16は、光学素子13（例えば、グランテーラープリズム）をもって直線偏光性の紫外線17に変換され、延伸などの方法により作製された一軸性屈折率楕円体のフィルムまたは／および二軸性屈折率楕円体のフィルム15上に塗布（コート）された感光性の重合体ないしは感光性の重合体と低分子化合物の混合体の膜14を照射する。実施例1および実施例2は、本発明の製造法により、光学異方素子を作製した実施例である。該光学異方素子の位相差の角度依存性は、偏光子、1／4波長板および検光子を用いたセナルモン法により所定の光学系で測定試料を回転させながら検光子の消光角を測定することにより求めた。

【0020】（実施例1）
（1）3．75重量％の重合体1および1．25重量％の低分子化合物1をジクロロエタンに溶解し、面内の位相差が81nmであるポリカーボネートフィルム上に約1．5μmの厚さで塗布し製膜した。
（2）製膜したフィルムの製膜面側に、グランテーラー

プリズムを用いて直線偏光に変換した紫外線を電界振動方向がポリカーボネートフィルムの延伸方向と一致するようにし、製膜面法線方向に対して２０度傾斜する方向から１００ｍＪ／ｃｍ²照射した。
（３）続いて、ポリカーボネートフィルム裏面側から２００ｍＪ／ｃｍ²１８０度対称に照射した。
（４）照射を終えたフィルム（膜）を１００℃に加熱した後、室温まで冷却した。
このようにして得られた光学異方素子の位相差は、図４に示すような角度依存性を有していた。
【００２１】（実施例２）
（１）３．７５重量％の重合体１および１．２５重量％の低分子化合物１をジクロロエタンに溶解し、面内の位相差が８１ｎｍであるポリカーボネートフィルム上に約１．５μｍの厚さで塗布し製膜した。
（２）製膜したフィルムの製膜面側に、グランテーラープリズムを用いて直線偏光に変換した紫外線を、電界振動方向がポリカーボネートフィルムの延伸方向と直交するようにし、製膜表面の法線方向に対して２０度傾斜する方向から１００ｍＪ／ｃｍ²照射。
（３）続いて、ポリカーボネートフィルム裏面側から２００ｍＪ／ｃｍ²１８０度対称に照射した。
（４）照射を終えたフィルム（膜）を１００℃に加熱した後、室温まで冷却した。
このようにして得られた光学異方素子の位相差は、図５に示すような角度依存性を有していた。
【００２２】カシオ製液晶カラーテレビＥＶ－５１０の偏光シートを剥がし、図６に示すように、実施例１による光学異方素子（フィルム）６１、６１’を、液晶セル６２の上下に各１枚貼り合わせ、次いで、偏光シート６３、６３’を上下１枚ずつ貼り合わせた。図において、ａ、ａ’は屈折率楕円体の傾斜方向を示し、ｂ、ｂ’はポリカーボネートフィルムの延伸方向を示し、ｃ、ｃ’は液晶セルのプレチルト方向を示し、ｄ、ｄ’は偏光シートの吸収軸方向を示す。光学異方素子６１、６１’は、それぞれ基材６１ｂ、６１ｂ’に斜め配向層６１ａ、６１ａ’を積層してなる。このような構成で液晶カラーテレビを駆動し、白表示および黒表示した場合のコントラスト比が5になるところを視野角と定義し、左右上下方向の視野角特性を測定した。コントラスト比の測定には、トプコン製ＢＭ－5Aを用いた。結果をまとめて表１に示す。

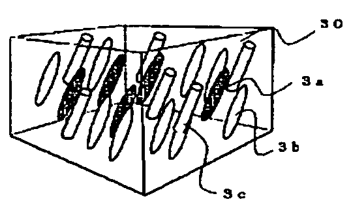
【表１】

表1

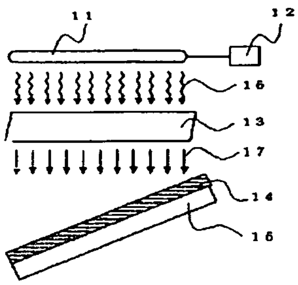
フィルム	視野角(°)			
	上	下	左	右
実施例1	5	48	63	63
実施例2	5	42	60	52
比較例(偏光シートのみ)	5	20	40	33

本発明の光学異方素子およびその製造法では、偏光露光により位相差を生じた素子に、更に紫外線を照射することにより未反応の感光性基の光反応を促進させ、素子中の配向を強固に固定することができる。このような光学異方素子は、耐熱性、光安定性に優れ実用に充分であった。実施例１、実施例２の光学異方素子ともに、下、左、右、方向で視野角拡大効果が確認された。
【発明の効果】従来、液晶表示装置において視野角拡大用の光学異方素子として活用できるような、光軸の傾斜した光学素子の製造工程には、煩雑な工程が必要であったが、本発明により、一軸性屈折率楕円体層または／および二軸性屈折率楕円体層に塗布した感光性の重合体ないしは感光性の重合体と低分子化合物の混合体の膜に斜め方向から偏光露光するという簡便な操作で光学異方素子の製造が可能となった。
【００２３】
【図面の簡単な説明】
【図１】本発明の光学異方素子の製造方法を示す概念図
【図２】偏光露光により感光した側鎖の模式図
【図３】偏光露光後の分子運動により配列した側鎖の模式図
【図４】実施例１の光学異方素子の位相差角度依存性
【図５】実施例２の光学異方素子の位相差角度依存性
【図６】視野角特性評価時の光学系
【００２４】
【符号の説明】
１１・・・紫外線ランプ
１２・・・電源
１３・・・光学素子（グランテーラープリズム）
１４・・・膜（フィルム）
１５・・・一軸性屈折率楕円体層または／および二軸性屈折率楕円体層
１６・・・無秩序光
１７・・・直線偏光性の紫外線

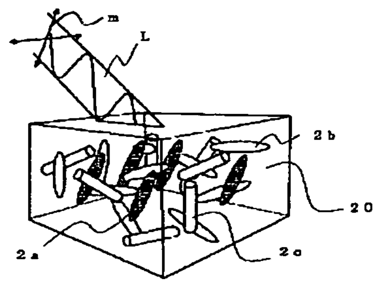
【図３】



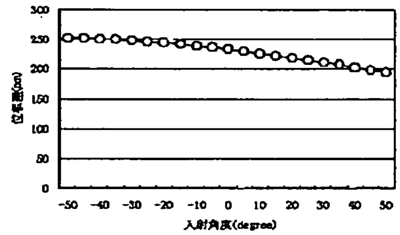
【図1】



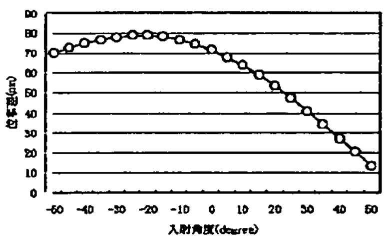
【図2】



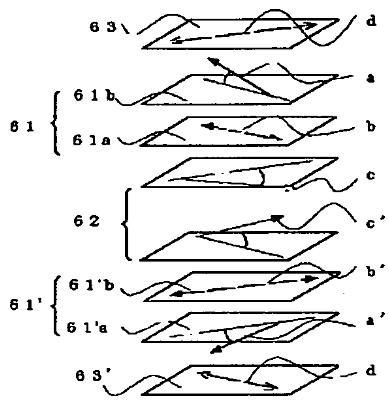
【図4】



【図5】



【図6】



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